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Analysis of Low Lead and Cadmium Concentrations in Soil Extracts by Graphite Furnace Atomic Absorption Spectrophotometry

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ABSTRAK

Satu kaedah analisis diperolehi untuk membolehkan pengukuran tepat kepekatan plumbum (Pb) dan kadmium (Cd) yang rendah dalam ekstraks tanah menggunakan spektrofotometer serapan atom relau grafit (GFAAS). Berdasarkan kepada pengukuran luas puncak bersama dengan pembetulan latar belakang, penggunaan asid fosforik 2% sebagai pengubahsuai kimia membolehkan GFAAS mengukur kepekatan Pb dan Cd serendah 3 μg dm^{-3} dengan darjah kepersisan yang tinggi. Bahan pengubahsuai kimia ini mempastikan penghasilan satu puncak pengatoman yang unggul bagi analit, dan dengan itu pengukuran kepekatan adalah tepat serta mempunyai kepekaan yang tinggi.

ABSTRACT

An analytical procedure was derived to provide an accurate measurement of low lead (Pb) and cadmium (Cd) concentrations in soil extracts using graphite furnace atomic absorption spectrometry (GFAAS). Based on peak area measurements and with background correction, the use of 2% phosphoric acid as chemical modifier enables the GFAAS to give measurements of Pb and Cd concentration as low as 3 μg dm^{-3} with a high degree of precision. The modifier ensures a single well-defined atomization peak of the analyte, and therefore higher sensitivity and accuracy in the measurements.

Keywords: cadmium; chemical modifier; GFAAS; lead; soil extracts

INTRODUCTION

The conventional flame atomic absorption spectrophotometer (FAAS) is widely used for the determination of lead, cadmium and other heavy metals in various matrices. The detection limit of the instrument, however, is about 1 mg dm^{-3} (parts per million) for most metals (Ure 1990) and thus is not sensitive enough for concentration values in the μg dm^{-3} (parts per billion) level. Consequently, for samples with low metal concentrations (e.g., water, plant and soil extracts) there is a tendency to express the measured concentration to the nearest parts per million (ppm) or simply record as "not detectable" (e.g., Shaw *et al.* 1984). This definitely gives a false (inaccurate) concentration data for the metal in question.

The recent introduction of graphite furnace atomic absorption spectrometry (GFAAS) has greatly enhanced the capability to measure metal in the parts per billion (ppb) range of concentration. The sensitivity of GFAAS is considered to be 100-1000-fold greater than FAAS (Ure 1990). GFAAS also has the advantage of requiring small (5-50 microlitres) samples. Despite these two significant merits, the application of GFAAS is not free from analytical problems. The atomic absorption signal of a particular metal can be susceptible to interferences arising from molecular and non-atomic absorption (i.e., background effect) and chemical interaction between the analyte and its matrix (i.e., chemical interference). These interferences can lead to erroneous measurement of the analyte concentration, and are more pronounced when the matrix is highly heterogeneous (Matousek 1982; Beaty 1987; Ure 1990).

This study reports on a procedure to minimize effectively the above interferences during the measurement of lead and cadmium in samples with a heterogeneous matrix such as those of soil extracts.

MATERIALS AND METHODS

The preparation of a soil extract involved equilibrating, in duplicate, 10 g of mine-contaminated soil sample with 50 cm^3 of equimolar (0.005M) $CaCl_2$ and $Ca(NO_3)_2$ electrolyte solution (*c.* 0.01M Ca) for 14 days under aerobic conditions. The equilibrated soil suspension was centrifuged, and filtered through 0.2 μm membrane filter. The filtrate was acidified with HNO_3 prior to Pb or Cd analysis.

The analysis of Pb and Cd was carried out using GFAAS (Varian Spectra AA-20 with a GTA-96 graphite tube atomizer). The main components of the instrument are a spectrometer, a programmable graphite tube furnace, a programmable sample dispenser and a computer processor with visual display unit. A series of optimization procedures was first performed to resolve the respective optimum GFAAS working conditions for the analysis of lead and cadmium. This included the selection of the optimum atomization temperature by producing a plot of absorbance versus temperature based on peak area and peak height measurements of the atomic absorption signal. To eliminate the background effect, the deuterium background correction system of the instrument was switched on.

One approach to overcoming the interference to absorption signals is the use of an appropriate chemical modifier (Matousek 1982; May and Brumbaugh 1982). The effectiveness of ammonium oxalate, ethylenediaminetetra-acetic acid (EDTA) and phosphoric acid, each of 2% (w/v) concentration, as chemical modifiers with Pb or Cd absorption signal (absorbance) was therefore examined. The absorbance of an aqueous Pb or Cd solution (20 microlitres) was determined each time when 2

microlitres of a modifier was added to the sample. These microsamples of the solutions were dispensed automatically into the graphite tube by the sample dispenser. The readings obtained were compared with the absorbance value obtained when deionised-distilled water was used in place of the modifier. The most suitable modifier was subsequently tested on Pb and Cd in selected soil extracts.

Finally, the calibration curves for both Pb and Cd were determined for the concentration ranges 0-100 $\mu g\ dm^{-3}$ and 0-25$\mu g\ dm^{-3}$, respectively. The respective solutions were prepared from 1000 mg dm^{-3} commercial standard, acidified with HNO_3 and diluted using 0.01M Ca electrolyte. The concentrations of Pb and Cd in a series of soil extracts of various Pb- and Cd-polluted soils were subsequently determined. Internal dilutions were carried out where necessary.

RESULTS AND DISCUSSION

The optimum GFAAS working conditions obtained for both Pb and Cd are specified in Table 1. The optimum atomization temperature was 2000 and 1800°C for Pb and Cd respectively, and for both metals peak area measurement of absorption signal was preferred over peak height. Establishment of the optimum atomization temperature is crucial in order to achieve the optimum absorbance reading (*Fig. 1*). Absorbance (peak height) generally increases with temperature until an optimum level is reached. By contrast, peak area absorbance first reached a maximum, at a relatively lower

TABLE 1
Optimum GFAAS working conditions for Pb and Cd analysis

Parameters	Lead	Cadmium
Instrument mode	Absorbance	Absorbance
Calibration mode	Concentration	Concentration
Measurenment mode	Peak area	Peak height
Sample introduction	Sampler automixing	Sampler automixing
Lamp current (mA)	5	4
Slit width (nm)	0.5	0.5
Wavelength (nm)	283.3	228.8
Time constant	0.005	0.005
Measurement time (s)	1.5	1.5
Replicates	2	2
Background correction	ON	ON
Furnace temperature (°C)		
Drying	120	120
Ashing	350	300
Atomization	2000	1800

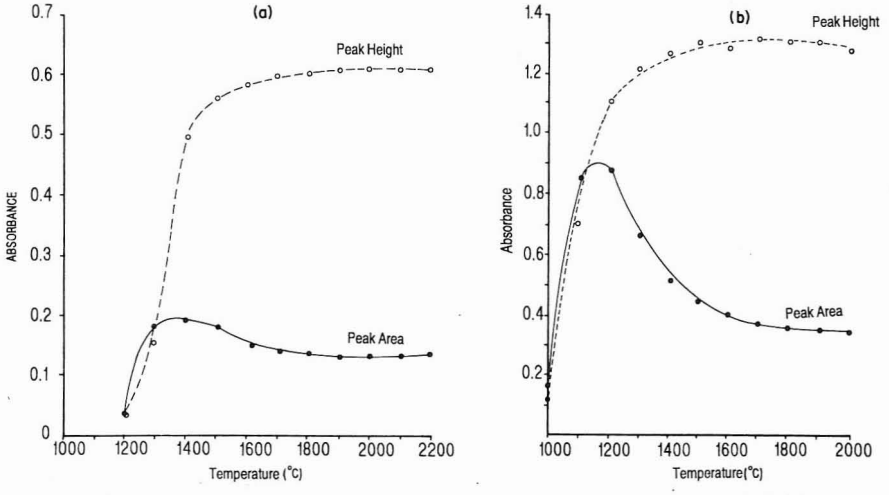


Fig. 1. Effect of atomization temperature on absorbance of (a) Pb and (b) Cd in aqueous solution, showing both the peak height and peak area measurements

temperature, then declined to an optimum value. During both modes of measurement, however, the optimum absorbance readings coincided with the same temperature. A maximum absorbance reading would not necessarily indicate an optimum atomization temperature, at least when peak area measurement was involved. This maximum reading was due to the broad and less symmetrical absorption signal (thus greater peak area) obtained, as shown for Cd in *Fig. 2.*

Peak height measurement of atomic signal gave a higher absorbance reading relative to peak area (*Fig. 1*); the difference was approximately 4X in both cases at optimum atomization temperature. Due to its lower reading, peak area was preferred over peak height for measurement of the absorbance. This would enable the extension of the calibration curve to higher concentrations, thereby avoiding excessive sample dilution. The analytical range for Pb, for example, using peak height absorbance was 2-25 $\mu g\ dm^{-3}$, which can be extended up to 150 $\mu g\ dm^{-3}$ using peak area absorbance (Jopony 1991).

The effect of the selected chemical modifiers on analyte absorbance is shown for Pb in *Fig. 3.* Ammonium oxalate and EDTA produced lower absorbance readings than deionised-distilled water. By contrast, H_3PO_4 produced a greater absorbance signal. Therefore, on the basis of absorbance readings, H_3PO_4 seemed to be the most suitable modifier among the three tested. Similar conclusions have also been derived for Cd (Jopony 1991). The primary goal of a chemical modifier is to isolate the analyte metal in a specific form that improves the separation between background and analyte atomic absorption signal. H_3PO_4 seemed to achieve this goal,

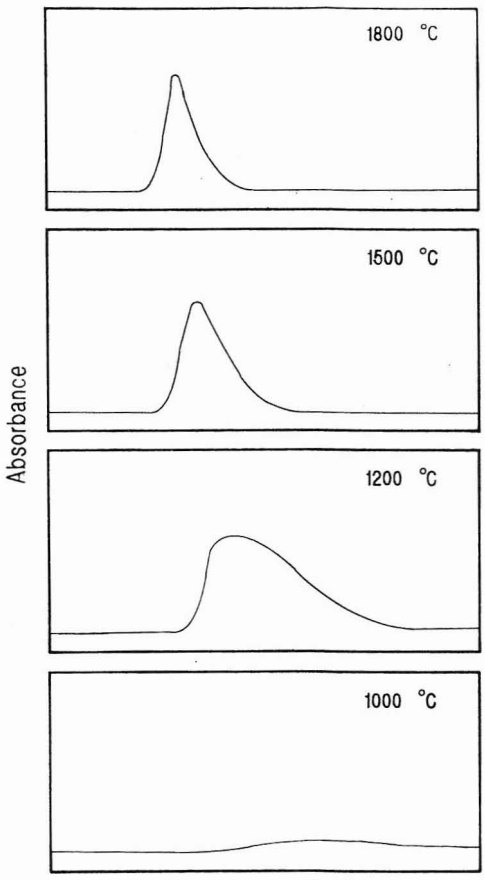


Fig. 2. Effect of atomization temperature on the absorption signal of an aqueous Cd solution

as shown in *Fig. 4*. The absorption signal for an aqueous metal solution was shifted and was also more symmetrical as a result of the modifier. The shift in the signal is an indication of the formation (precipitation) of a new compound (Czobik and Matousek 1977), which in this case is most likely to be metal-phosphate. *Fig. 4* also shows that the use of the background corrector resulted in a smooth base-line signal which, otherwise, would be a noisy one.

The suitability of H_3PO_4 as the chemical modifier is more pronounced in the soil extracts (*Fig. 5*). The addition of the modifier clearly resulted in well-defined absorption peaks. By contrast, without the modifier the absorption signal was generally broad with poor resolution of the peaks. The measured absorbance (peak area), therefore, was relatively higher and consequently the measured concentration would be erroneously higher than the 'true' values. The significance of H_3PO_4 as a modifier is

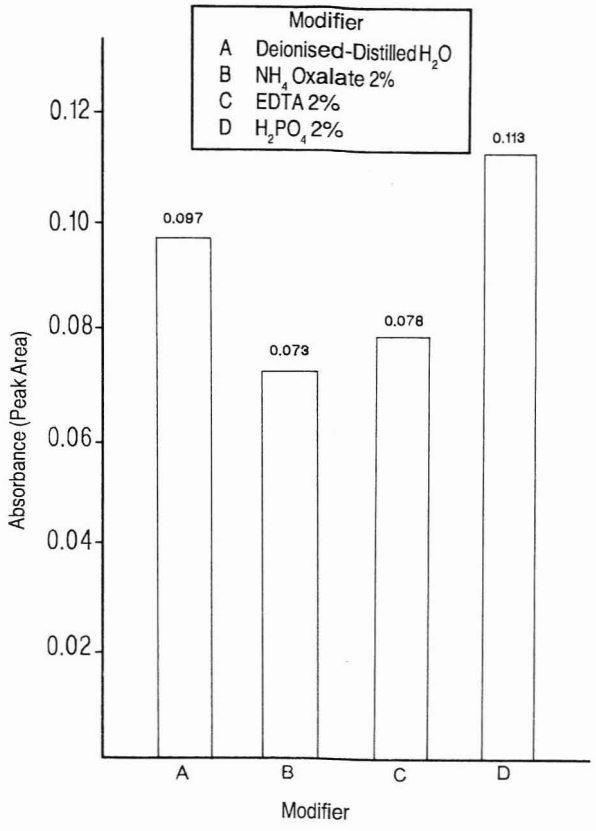


Fig. 3. Effect of different types of chemical modifier on the absorbance of an aqueous Pb solution

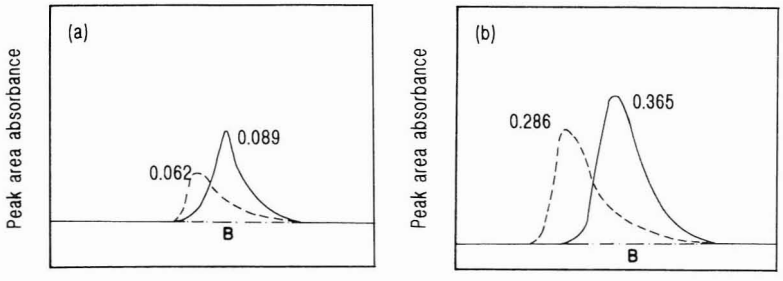


Fig. 4. Absorption signals of (a) Pb and (b) Cd in aqueous solution, with modifier (———) and without modifier (- - - - -). B represents the baseline signal in the presence of H_3PO_4 modifier

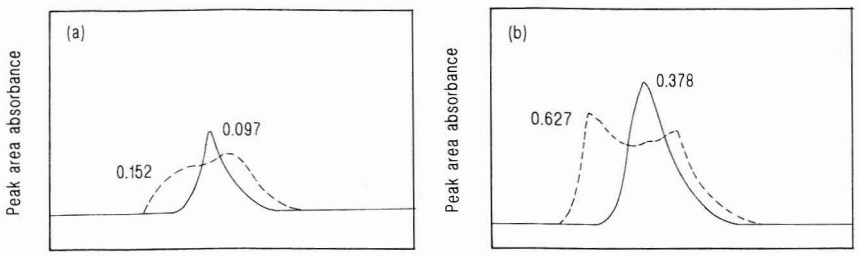


Fig. 5. Absorption signals of (a) Pb and (b) Cd in soil extracts, with modifier (———) and without modifier (- - - - -)

also demonstrated by the high precision (absorbance) obtained for the calibration graphs (*Fig. 6*), as indicated by the very small RSD values recorded by duplicate atomizations.

The significance of the modifier (H_3PO_4) in the analysis of Pb and Cd in soil extracts is shown in Table 2. Only selected samples of comparable Pb and Cd concentrations are presented to illustrate the wide range of

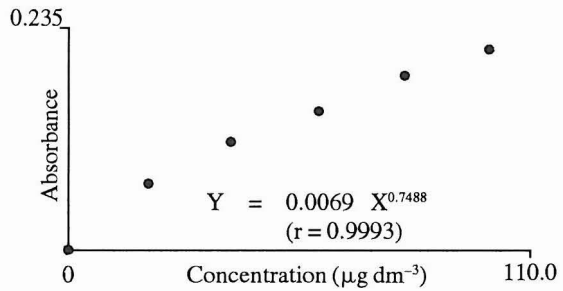
TABLE 2
Selected examples of Pb and Cd concentrations in soil extracts as measured by GFAAS

Lead		Cadmium	
Concentration ($\mu g\ dm^{-3}$)	%CV	Concentration ($\mu g\ dm^{-3}$)	%CV
3.1	2.0	3.0	3.3
4.9	7.2	4.5	4.4
6.9	5.8	6.7	7.5
12.6	6.1	12.7	1.6
16.4	0.9	17.4	1.1
27.0	5.3	29.3	1.0
43.7	3.6	43.6	9.8
53.8	1.4	51.9	0.4
92.7	2.4	93.9	2.2
109.8	3.7	107.5	5.0
173.3	2.6	174.8	0.7
201.7	1.9	203.6	5.3
263.0	0.8	265.1	2.0
313.4	2.3	347.5	6.1

%CV = percent coefficient of variation
= (Standard Deviation x 100) / mean

(a) Lead

Cone ($\mu g\ dm^{-3}$)	Readings		Mean Abs	% RSD
0	0	0	0	
20.0	0.064	0.065	0.064	1.2
40.0	0.113	0.110	0.112	1.7
60.0	0.150	0.150	0.150	0.1
80.0	0.184	0.183	0.183	0.9
100.0	0.214	0.214	0.214	0.1



(b) Cadmium

Cone ($\mu g\ dm^{-3}$)	Readings		Mean Abs	% RSD
0	0	0	0	
5.0	0.184	0.179	0.182	2.2
10.0	0.283	0.277	0.280	1.6
15.0	0.359	0.359	0.359	0.0
20.0	0.424	0.412	0.418	2.1
25.0	0.456	0.461	0.458	0.7

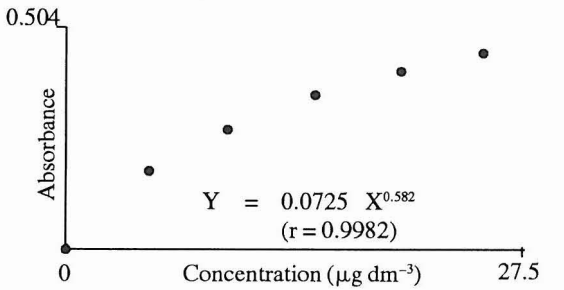


Fig. 6. Typical GFAAS calibration graphs for (a) Pb and (b) Cd for the concentration range 0 - 100 $\mu g\ dm^{-3}$ and 0 - 25 $\mu g\ dm^{-3}$ respectively

concentrations involved. The values for duplicate samples, each with duplicate atomization, are generally almost identical, as indicated by the low coefficient (%) of variation. The measurements have a high degree of precision and reproducibility.

CONCLUSION

The analysis of low Pb and Cd concentrations in samples with heterogeneous matrices by GFAAS can be greatly improved in terms of accuracy and sensitivity by using a suitable chemical modifier such as phosphoric acid, as in the case of soil extracts, under optimum instrumental conditions. Failure to eliminate the interferences to the atomic absorption signal produces erroneously high analyte concentration measurements.

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